Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Orthogonal smectic and nematic ordering in three-ring polar bent-core molecules with anti-parallel arrangement

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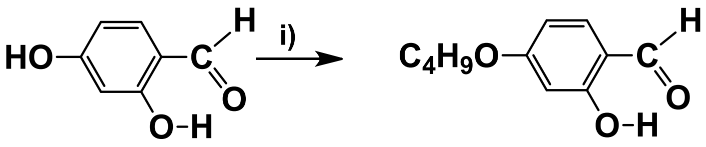
Table of contents:

1. **Synthesis:**

Step 1.

The synthesis of 4-n-alkoxy-2-hydroxybenzaldehyde was performed by using a modification of the literature procedure [1,2] to improve the product and yield.



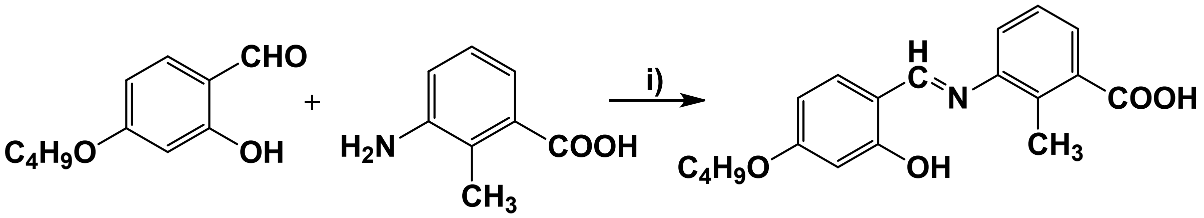
Scheme 1: i) acetone(dry), $KHCO_3$, C_4H_9Br , KI, reflux, 36 h

2, 4-dihydroxybenzaldehyde (6.9 g, 50 mmol), 1-bromobutane (6.6g, 50 mmol), $KHCO_3$ (1g, 50mmol) and catalytic amount of KI were mixed in dry acetone (250 mL) and the mixture was refluxed for 36 h. It was then filtered hot to remove the insoluble solid. The warm solution was neutralized by adding dilute HCl and extracted twice with $CHCl_3$ (100 mL). The combined extract was concentrated to give a purple liquid. The product was further purified by column chromatography using silica gel (60-120 mesh) eluting with a mixture of hexane and chloroform (v/v 1:1) followed by evaporation of the solvent. The product was obtained as a pale yellow liquid. Yield: 5.8 g (60 %); IR υ_{max} in cm-1: 3449 (ν O-H, H-bonded), 1666 (ν C=O, aldehyde). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 11.41 (s, 1H, -OH), 9.66 (s, 1H, -CHO), 7.41 (d, 1H, J = 8.7 Hz, ArH), 6.53 (d, 1H, J = 8.7 Hz, ArH), 6.62 (d, 1H, J = 2.7Hz, ArH), 4.03 (t, 2H, J = 7.8 Hz, $-OCH_2-$), 1.65-1.20 (m, 4H, $-(CH_2)_2-$), 0.89 (t, 3H, J = 6.6 Hz, $-CH_3$).

The other homologues with varying the number of methylene units with carbon atoms (n) in the alkoxy chain (n = 6, 8, 10, 12) were synthesized following the above procedure with appropriate amount of alkyl bromides.

Step 2.

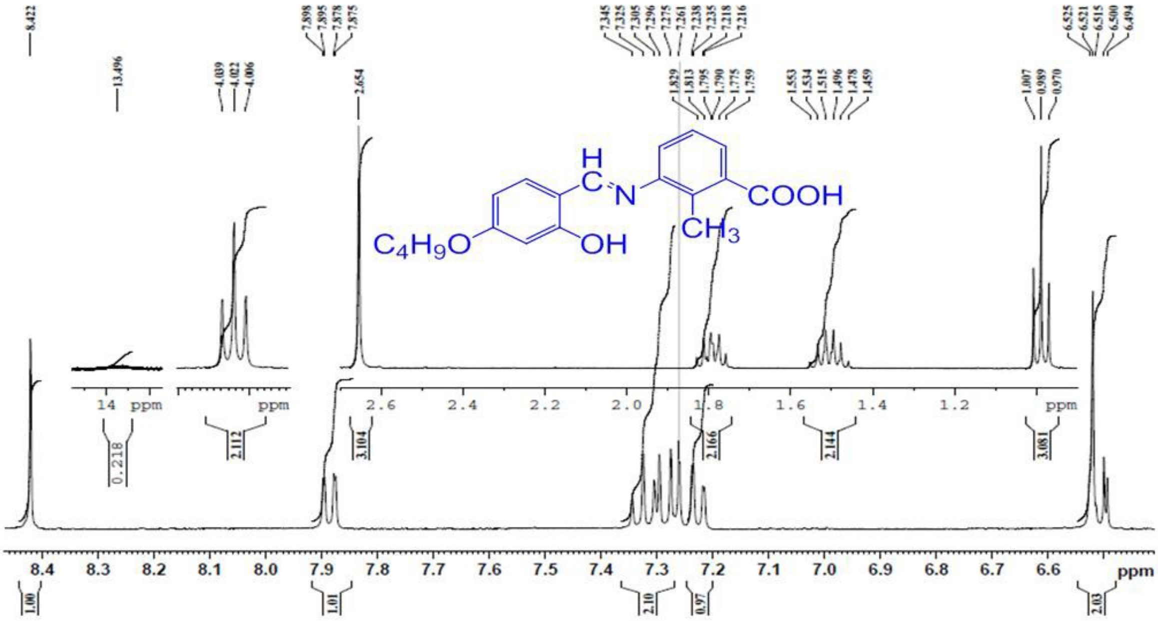
The intermediate Schiff base compounds were synthesized following the standard procedure reported earlier [3,4] by refluxing a mixture of ethanolic solution of 1 mmol of the 4-n-butyloxy-2-hydroxybenzaldehyde with 1 mmol of 3-amino-2-methyl-benzoic acid and few drops of glacial acetic acid as catalyst for 4 h. The precipitated product was purified by repeated recrystallization from absolute ethanol. Yellow solid. Yield: 0.85 g, (78%).



Scheme 2: i) absolute alcohol, glacial acetic acid, reflux, 4h

Elemental analysis calculated for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28%; Found C, 69.54 %; H, 6.43; N, 4.09%. IR (υ_{max} in cm^{-1}): 3516 (ν O-H), 1687 (ν C=O, acid), 1614 (ν C=N, amine). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 13.49 (s, 1H, - OH), 10.06 (s, 1H, -COOH), 8.42 (s, 1H, -CH=N-), 7.88 (dd, 1H, J = 1.2 Hz, J = 8.0 Hz, ArH), 7.32 (t, 1H, J = 8.0 Hz, ArH), 7.28 (d, 1H, J = 8.4 Hz, ArH), 7.22 (dd, 1H, J=1.2 Hz ,J=8.0 Hz, ArH), 6.52 (d, 1H, J = 2.4 Hz ,J = 8.4 Hz, ArH), 6.49 (s, 1H, J = 2.4 Hz, ArH); 4.02 (t, 2H, J = 6.4Hz, $-OCH_2-$); 2.65 (s, 3H, $ArCH_3$); 1.80 (q, 2H, $-CH_2-$); 1.51 (m, 2H, $-CH_2-$); 0.99 (t, 3H, J =7.6 Hz, $-CH_3$).

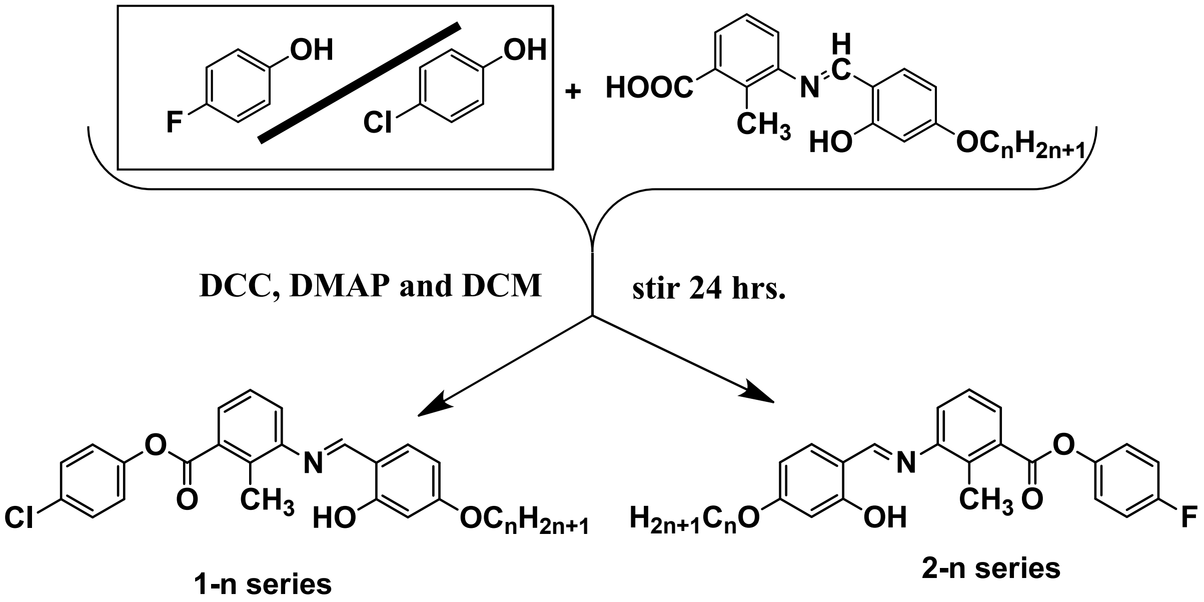
Using the same procedure as described in scheme 2, other compounds with varying the number of carbon atoms (n) in the alkoxy chain (n = 6, 8, 10, 12) were synthesized.



Step 3.

Appropriate quantity of methyl substituted benzoic acid (2-Methyl-3-N-(4-n-butyloxy-2-hydroxybenzylidene) amino benzoic acid, (0.32 g, 1 mmol) and 4-fluorophenol (0.11 g, 1mmol) were dissolved in dry dichloromethane (DCM) (50 mL) under nitrogen atmosphere and catalytic amount of 4-dimethylaminopyridine (DMAP) (4 mg, 0.02 mmol) was added to the solution. A solution of N, N dicyclohexylcarbodiimide (DCC) (0.21 g, 1mmol) was added to the reaction mixture and the mixture was stirred for 24 h under inert atmosphere at room temperature. The precipitate of N, N/-dicyclohexylurea was removed by filtration and the solvent DCM was evaporated to get crude yellow product. The yellow solid was recrystallized several times from methanol and absolute ethanol to get the pure product. (Yield= 80%)

Using the same procedure as described in scheme 3, all the compounds of 1-n and 2-n series with varying the number of alkyl chains were synthesized.



Scheme 3. n = 4, 6, 8, 10 ,12.

Characterization:

Compound **1-8**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1743 cm^{-1}, HC=N stretching of an imine at 1616 cm^{-1}

UV-Vis (nm): 290 nm, 339 nm

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.44-7.19 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.03 (t, 2H, J= 8,4Hz, -O-CH_2-), 2.68 (s,3H,Ar-CH_3), 1.86-1.79(m, 2H, -CH_2), 1.37-1.32(m,8H, -$(CH_2)_4$), 1.52-1.45 (m, 2H, -CH_2), 0.92 (t, 3H, J = 8.0 Hz, -CH_3)

^{13}C-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 14.13, 15.45, 22.68, 26.00, 29.07, 29.24, 29.34,31.83,68.35,101.54,107.80,112.96,122.77,123.15,126.62,128.36,129.59,130.20,131.34, 133.69,134.33,149.34,149.65,162.74,163.66,163.92,165.80.

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
1-8	494.2198	492.1942	494.2081	493.2020	0.00237

Compound **2-8**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1743 cm^{-1}, HC=N stretching of an imine at 1619 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, CDCl3, δ in ppm): δ = 13.53 (s, 1H, -OH), 8.47 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.41-7.13 (7H, Ar-H) , 6.55-6.53 (1H, Ar-H), 4.03 (t, 2H, J= 6.4 Hz, -O-CH_2-), 2.68 (3H, Ar-CH_3), 1.85-1.81(m, 2H, -CH_2), 1.37-1.32(m, 8H, -$(CH_2)_4$), 1.52-1.42 (m, 2H, -CH_2), 0.92 (t, 3H, J = 8.0 Hz, -CH_3)

^{13}C-NMR (400 MHz, CDCl3, δ in ppm): δ = 14.13, 15.46, 22.68, 26.00, 29.07, 29.24,29.34,31.83,68.35,101.55,107.80,112.97,116.08,116.32,122.69,123.12,123.21,126.61, 128.34,130.36,133.68,134.27,149.63,162.72,163.67,163.91,166.01

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
2-8	478.2393	476.2237	478.2498	477.2315	0.00220

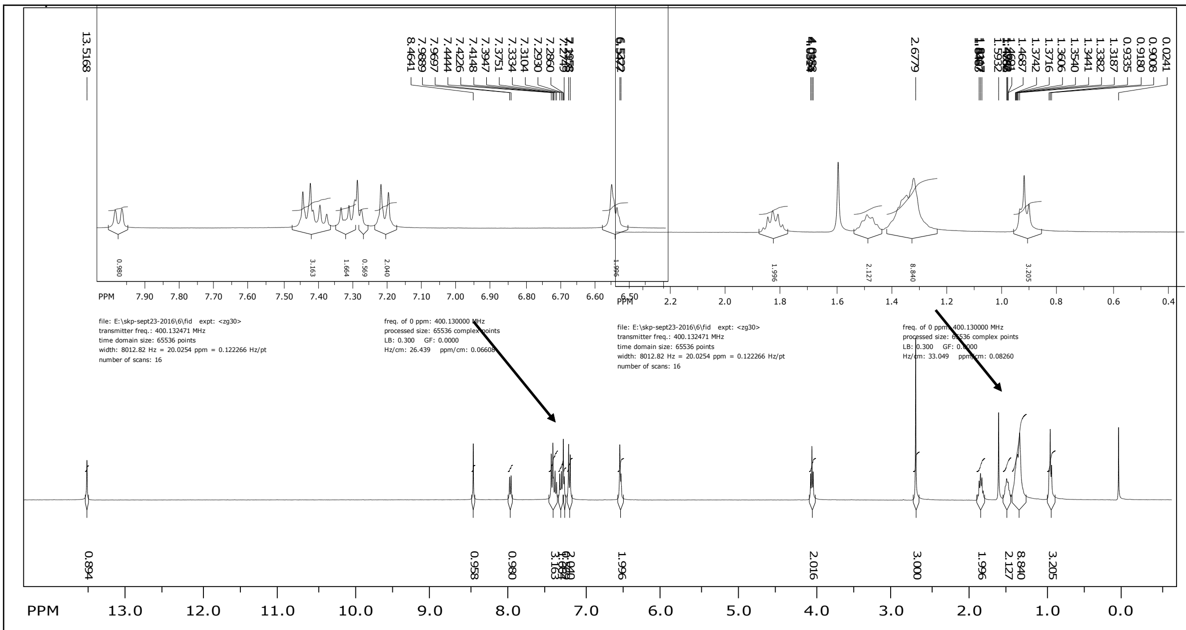


Figure S1. ^{1}H-NMR of compound 1-8.

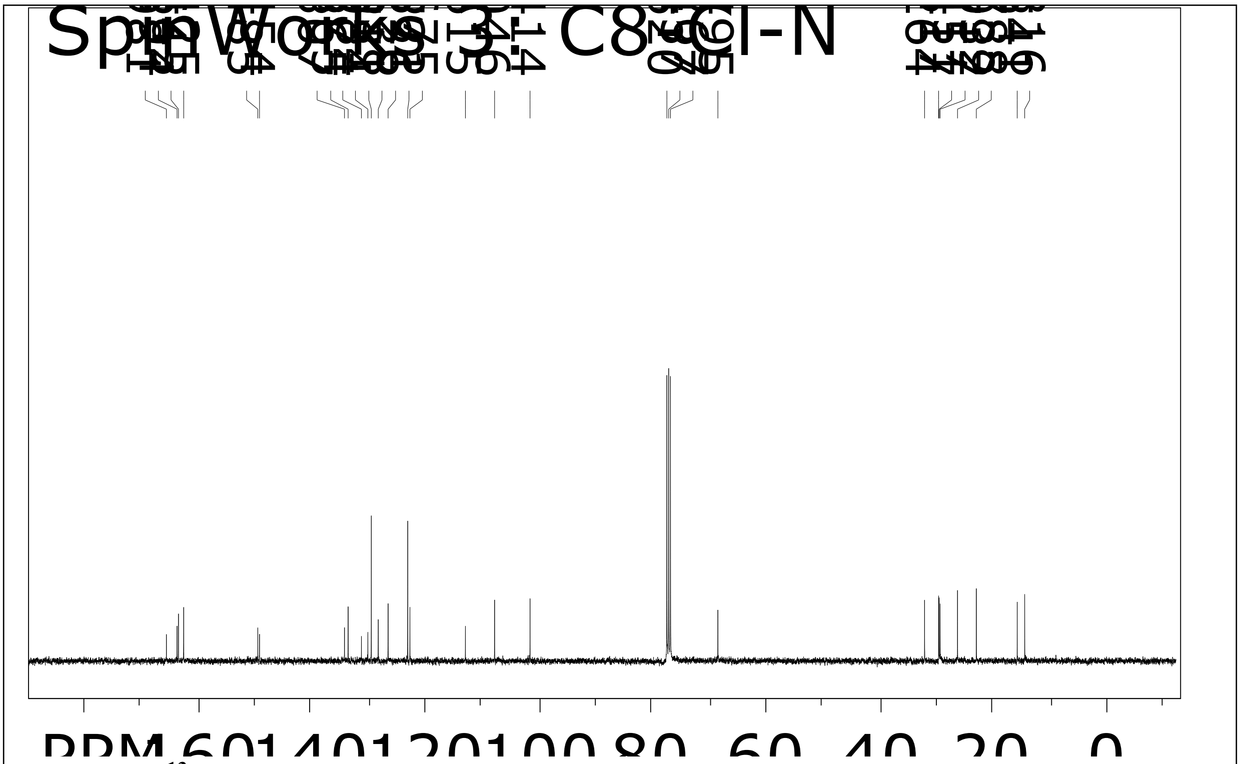


Figure S2. ^{13}C-NMR of compound 1-8.

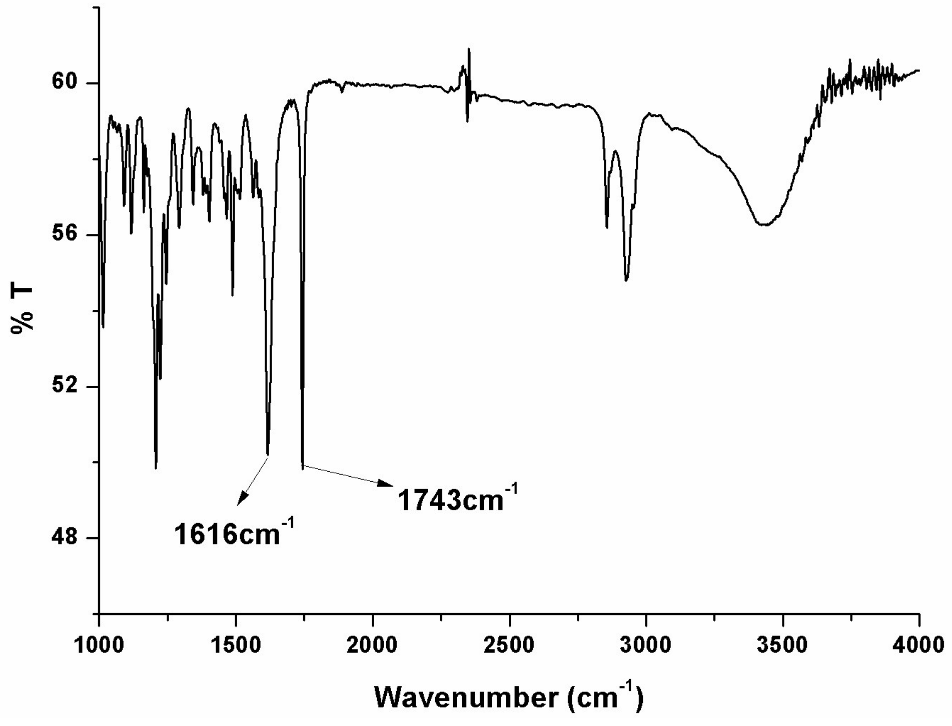


Figure S3. FT-IR of compound 1-8.

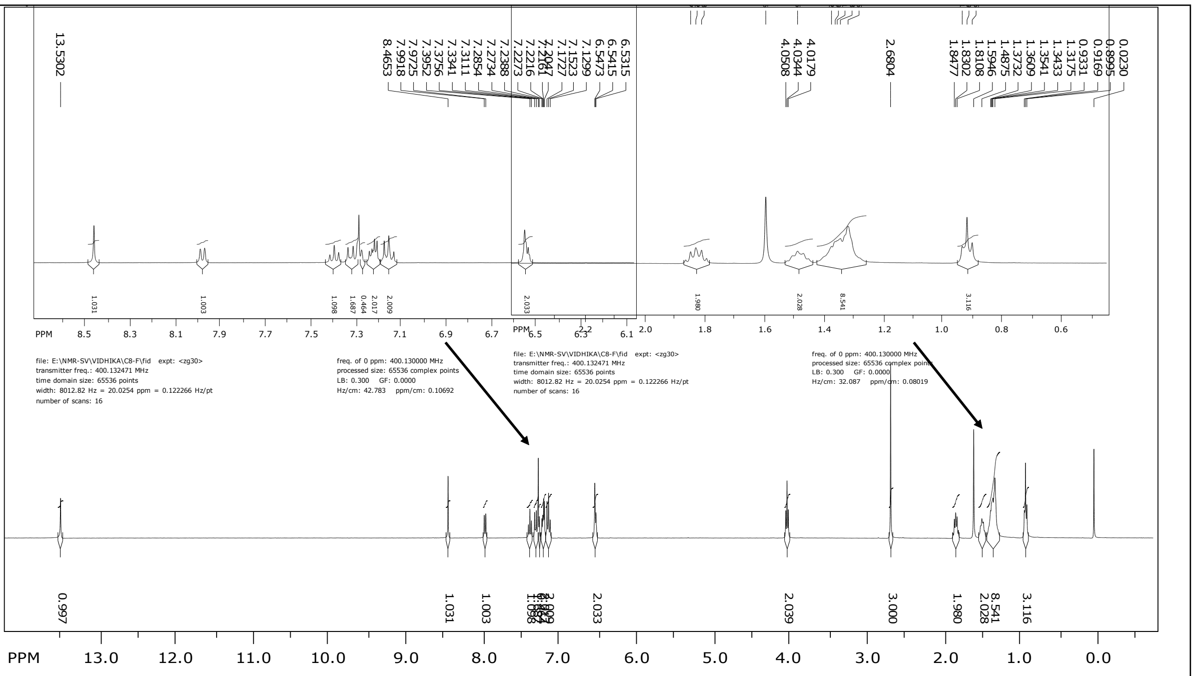


Figure S4. ^{1}H-NMR of compound 2-8.

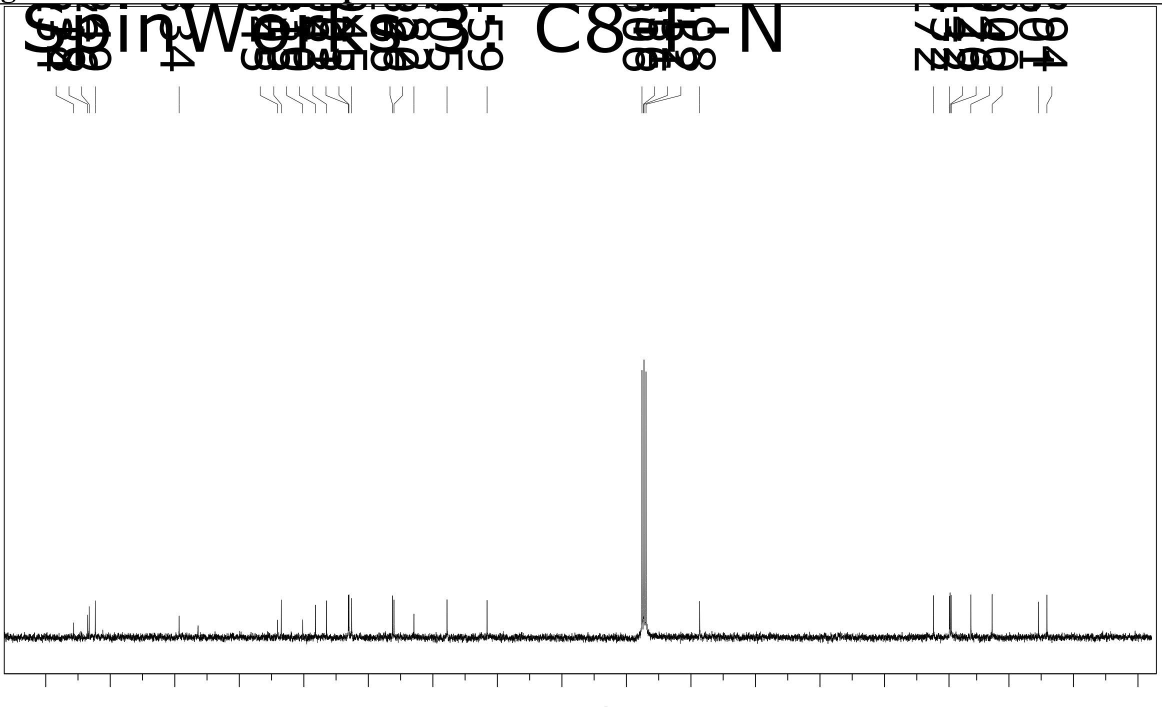


Figure S5. ^{13}C-NMR of compound 2-8.

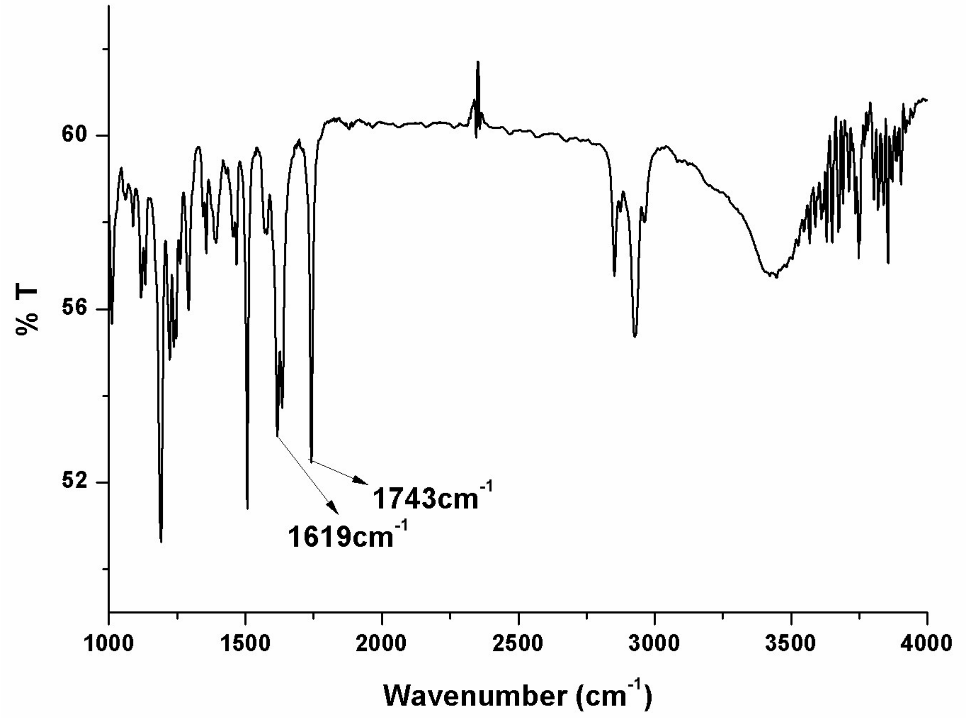


Figure S6. FT-IR of compound 2-8.

Compound **1-4**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1730 cm^{-1}, HC=N stretching of an imine at 1613 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, CDCl$_3$, δ in ppm): δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.44-7.19 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.05 (t, 2H, J= 4,8Hz, -O-CH$_2$-), 2.68 (s,3H,Ar-CH$_3$), 1.86-1.78(m, 2H, -CH$_2$), 1.56-1.50 (m,2H, -CH$_2$), 1.01 (t, 3H, J = 8.00 Hz, -CH$_3$)

^{13}C-NMR (400 MHz, CDCl$_3$, δ in ppm): δ = 14.06, 15.46 ,22.60, 25.68, 29.03, 31.56, 68.35, 101.53 ,107.81, 112.96, 116.08, 122.78, 123.15, 126.62, 128.36, 129.60, 131.34, 133.68, 134.27, 149.32, 149.66, 162.75, 163.66, 163.92, 165.82

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
1-4	438.1472	436.1316	438.1544	437.1394	0.00164

Compound **2-4**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1730 cm^{-1}, HC=N stretching of an imine at 1614 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.41-7.13 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.05 (t, 2H, J= 4,8Hz, -O-CH_2-), 2.67 (s,3H,Ar-CH_3), 1.86-1.78 (m, 2H, -CH_2), 1.56-1.50 (m,2H, -CH_2), 1.01 (t, 3H, J = 8 Hz, -CH_3)

^{13}C-NMR (400 MHz, $CDCl_3$, δ in ppm):δ = 14.13, 15.46, 22.68, 31.83, 68.35, 101.55, 107.80, 112.97, 116.08, 122.69, 123.12, 126.61, 128.34, 129.70, 130.36, 133.68, 134.27, 149.31, 149.63, 162.72, 163.67, 163.91, 166.01

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
2-4	422.1767	420.1611	422.1835	421.1689	0.00161

<u>Compound **1-6**</u>

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1}, HC=N stretching of an imine at 1640 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N),7.98 (d, 1H, J = 8.0 Hz, Ar-H), 7.44-7.19 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.04 (t, 2H, J= 8,4Hz, -O-CH_2-), 2.68 (s,3H,Ar-CH_3), 1.87-1.79 (m, 2H, -CH_2), 1.53-1.46 (m,2H, -CH_2), 1.39-1.36 (m, 4H, -$(CH_2)_4$), 0.94 (t, 3H, J = 8.0 Hz, -CH_3)

^{13}C-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 14.06, 15.46 ,22.60, 25.68, 29.03, 31.56, 68.35, 101.53 ,107.81, 112.96, 116.08, 122.78, 123.15, 126.62, 128.36, 129.60, 131.34, 133.68, 134.27, 149.32, 149.66, 162.75, 163.66, 163.92, 165.82

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
1-6	466.1785	464.1629	466.1898	465.1707	0.00242

<u>Compound **2-6**</u>

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1730 cm^{-1}, HC=N stretching of an imine at 1614 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.97(d, 1H, J = 8.0 Hz, Ar-H), 7.43-7.13 (7H, Ar-H) , 6.55-6.54 (2H, Ar-H), 4.04 (t, 2H, J= 4,8Hz, -O-CH2-), 2.67 (s,3H,Ar-CH3), 1.86-1.78 (m, 2H, -CH2), 1.56-1.50 (m,2H, -CH2), 1.36-1.30 (m, 6H, -$(CH_2)_3$), 0.91 (t, 3H, J = 8.0 Hz, -CH_3)

^{13}C-NMR (400 MHz, $CDCl_3$, δ in ppm):δ = 14.13, 15.46, 22.68, 26.00, 29.24, 31.83, 68.35, 101.55, 107.80, 112.97, 116.08, 122.69, 123.12, 126.61, 128.34, 129.70, 130.36, 133.68, 134.27, 149.31, 149.63, 162.72, 163.67, 163.91, 166.01

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
2-6	450.2080	448.1924	450.2167	449.2002	0.00193

Compound **1-10**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1754 cm^{-1}, HC=N stretching of an imine at 1629 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.44-7.19 (7H, Ar-H) , 6.55-6.52 (2H, Ar-H), 4.03 (t, 2H, J= 8Hz, -O-CH_2-), 2.68 (s,3H,Ar-CH_3), 1.86-1.79 (m, 2H, -CH_2), 1.52-1.45 (m,2H, -CH_2), 1.39-1.30 (m, 12H, -$(CH_2)_6$), 0.91 (t, 3H, J = 4.0,8.0 Hz, -CH_3)

^{13}C-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 14.14, 15.46, 22.68, 26.02, 29.07, 29.28, 29.37, 29.61, 29.76, 31.92, 68.36, 101.56, 107.81, 113.00, 116.08, 116.31, 122.79, 123.23, 123.56, 126.62, 128.39, 129.60, 130.21, 133.70, 149.69, 162.75, 163.66, 164.03, 165.76

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
1-10	522.2411	520.2255	522.2391	521.2333	-0.00038

Compound **2-10**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1746 cm^{-1}, HC=N stretching of an imine at 1621 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.52 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.44-7.19 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.04 (t, 2H, J= 8,4Hz, -O-CH_2-), 2.68 (s,3H,Ar-CH_3), 1.87-1.79 (m, 2H, -CH_2), 1.53-1.46 (m,2H, -CH_2), 1.39-1.36 (m, 4H, -$(CH_2)_4$), 0.94 (t, 3H, J = 8.0 Hz, -CH_3)

^{13}C-NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 14.14, 15.45, 22.70, 25.99, 29.07, 29.24, 29.33, 29.37, 29.57, 31.91, 68.34, 101.54, 107.80, 112.97, 116.08, 116.31, 122.69, 123.11, 123.20, 126.61, 128.34, 130.33, 133.67, 134.25, 149.64, 162.72, 163.66, 163.91, 166.10

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
2-10	506.2706	504.2550	506.2791	505.2628	0.00168

Compound **1-12**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1746 cm^{-1}, HC=N stretching of an imine at 1621 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, CDCl$_3$, δ in ppm): δ = 13.51 (s, 1H, -OH), 8.46 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.44-7.20 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.04 (t, 2H, J= 4,8Hz, -O-CH$_2$-), 2.68 (s,3H,Ar-CH$_3$), 1.86-1.79 (m, 2H, -CH$_2$), 1.50-1.45 (m,2H, -CH$_2$), 1.37-1.29 (m, 12H, -(CH$_2$)$_6$), 0.91 (t, 3H, J = 4,8 Hz, -CH$_3$)

^{13}C-NMR (400 MHz, CDCl$_3$, δ in ppm): 14.14, 15.46, 22.68, 26.02, 29.07, 29.24, 29.37, 29.58, 29.61, 29.66, 29.68, 31.92, 68.36, 101.56, 107.81, 113.00, 116.08, 116.31, 122.79, 123.23, 123.56, 126.62, 128.39, 129.60, 130.21, 133.70, 149.69, 162.75, 163.66, 164.03, 165.76

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
1-12	550.2724	548.2568	550.2791	549.2646	0.00122

Compound **2-12**

FT-IR (cm^{-1}): Intramolecular H-bonding of O-H….N at 3170–3400 cm^{-1}, C=O stretching band of ester at 1746 cm^{-1}, HC=N stretching of an imine at 1629 cm^{-1}

UV-Vis (nm): 289 nm, 339 nm

^{1}H-NMR (400 MHz, CDCl$_3$, δ in ppm): δ= 13.52 (s, 1H, -OH), 8.47 (s, 1H, -CH=N), 7.98(d, 1H, J = 8.0 Hz, Ar-H), 7.41-7.13 (7H, Ar-H) , 6.55-6.53 (2H, Ar-H), 4.03 (t, 2H, J= 8 Hz, -O-CH$_2$-), 2.68 (s,3H,Ar-CH$_3$), 1.86-1.79 (m, 2H, -CH$_2$), 1.50-1.45 (m,2H, -CH$_2$), 1.37-1.29 (m, 16H, -(CH$_2$)$_8$), 0.91 (t, 3H, J = 8,4 Hz, -CH$_3$)

^{13}C-NMR (400 MHz, CDCl$_3$, δ in ppm): δ = 14.15, 15.46, 22.72, 25.99, 29.07, 29.24, 29.37, 29.58, 29.61, 29.66, 29.68, 31.94, 68.35, 101.53, 107.80, 112.96, 116.08, 116.31, 122.70, 123.12, 123.20, 126.61, 128.34, 130.33, 133.67, 134.26, 149.63, 162.72, 163.66, 163.91, 166.01

Compound	M+H	M-H	Observed Mass	Exact Mass	% error
2-12	534.3019	532.2863	534.3151	533.2941	0.00247

2. UV-Vis spectra:

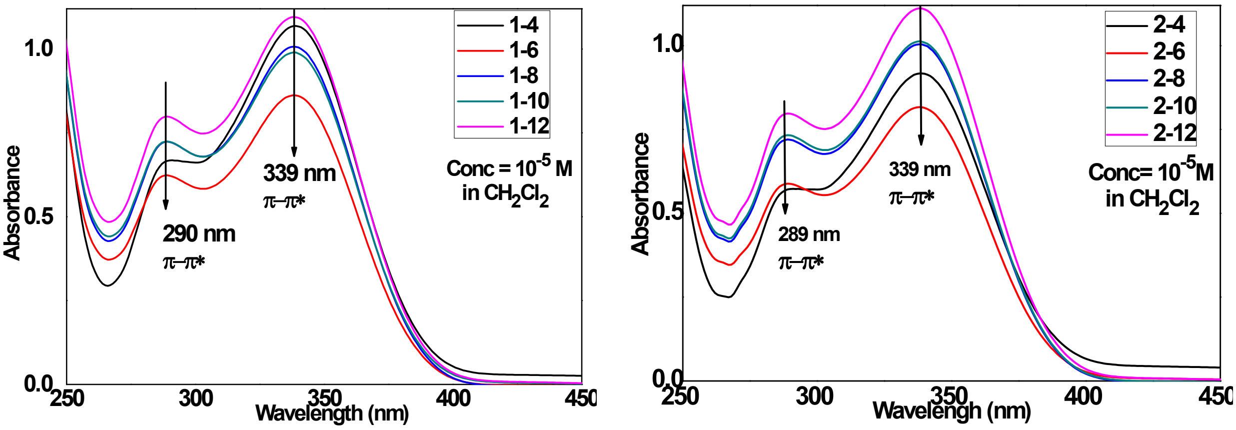


Figure S7. (a) UV-Visible of 1-n series. (b) UV-Visible of 2-n series.

3. Polarizing optical microscope:

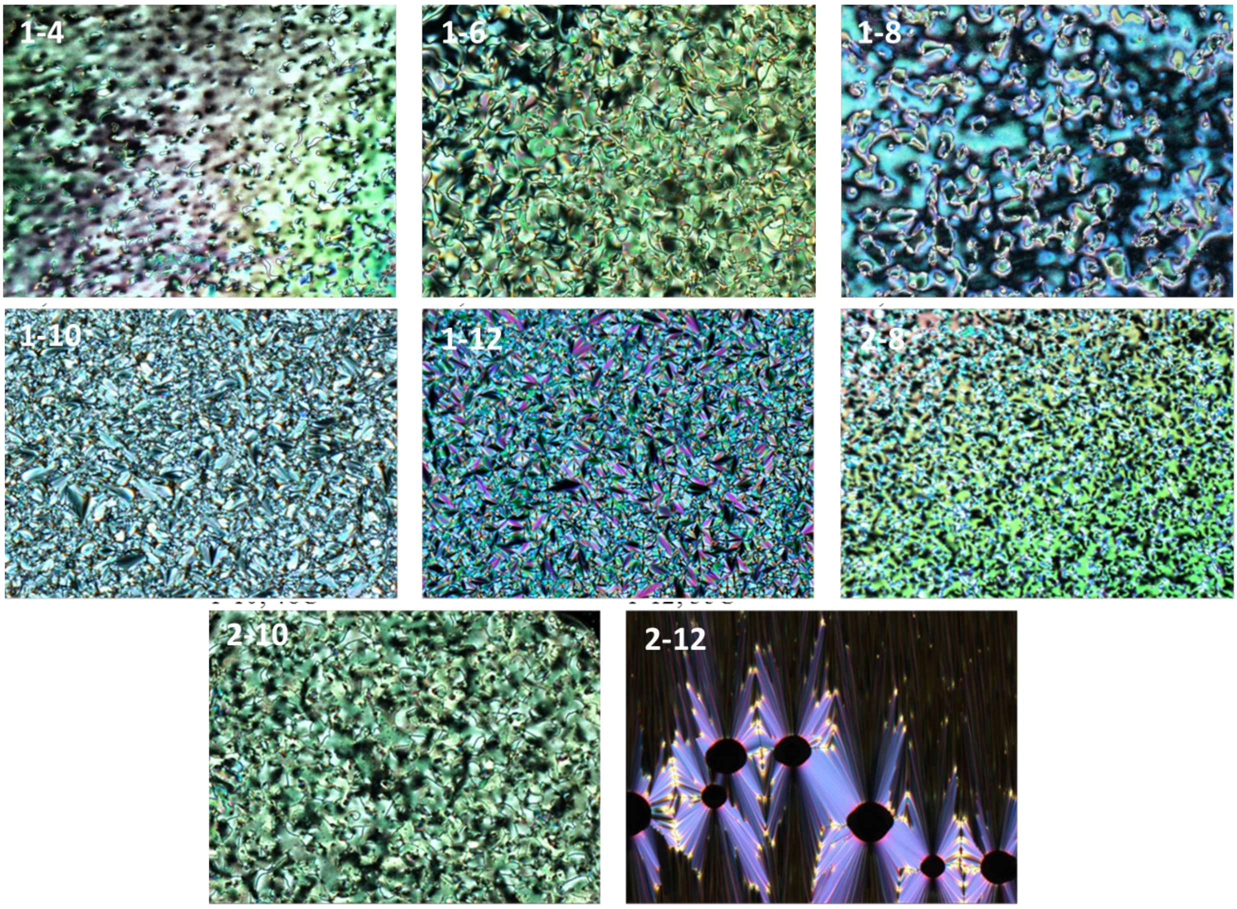


Figure S8. Optical textures observed by POM for all the compounds; 1-4, 1-6, 1-8, 2-8, 2-12 showing nematic phase and 1-10, 1-12, 2-12 showing smectic phase.

4. Differential scanning calorimetry:

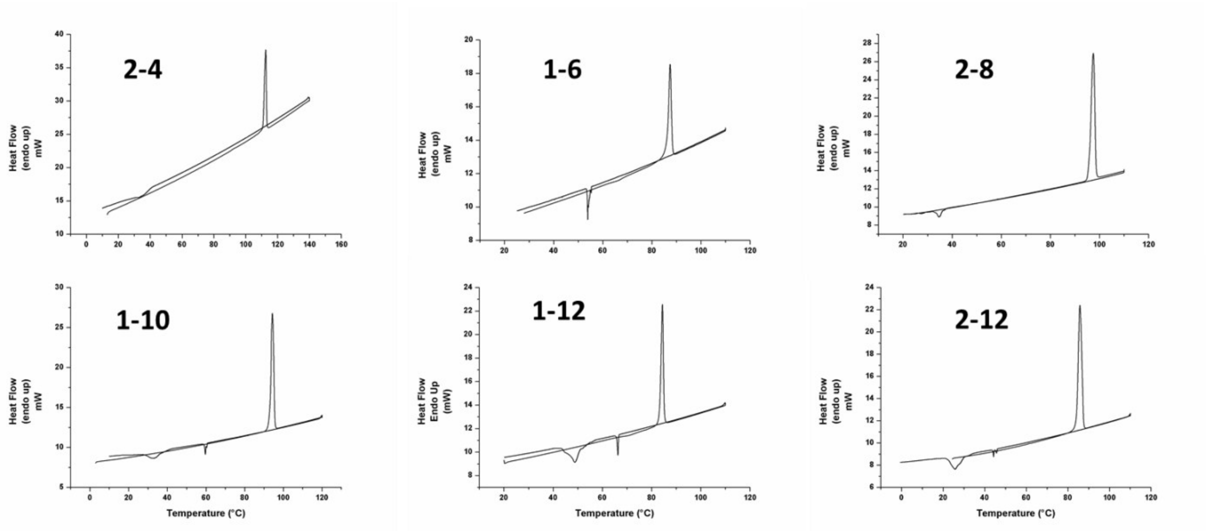


Figure S9. DSC thermogram of the synthesized compounds.

5. X-ray diffraction:

Table S1: Temperature (°C) vs d-spacing (Å) for compound 1-12 (see Fig. 5b of main paper)

Temperature (˚C)	d-spacing (Å)
66	35.393
65	35.393
64	35.430
63	35.398
62	35.414
61	35.393
60	35.398
59	35.429
58	35.378
57	35.406
56	35.421
55	35.399
54	35.415
53	35.406
52	35.403
51	35.399

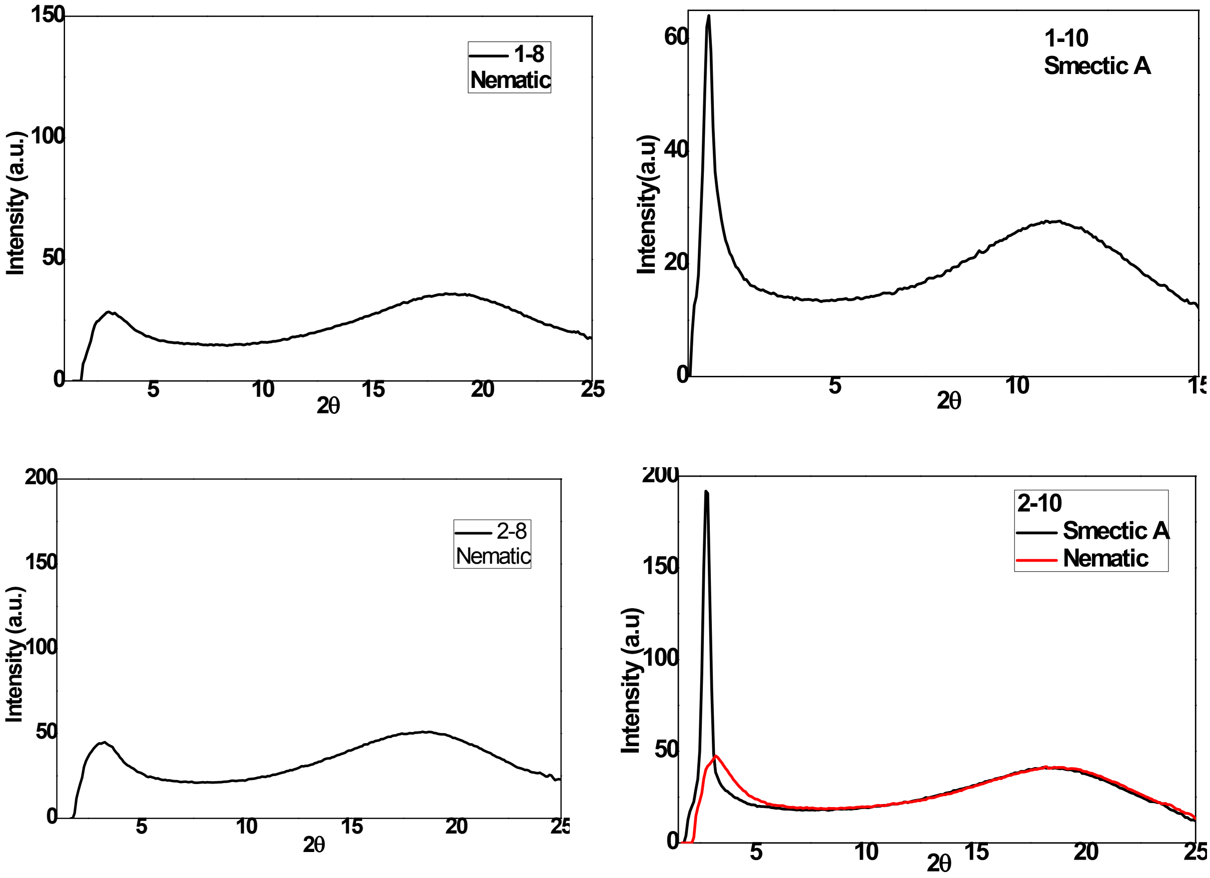


Figure S10. XRD profile of the three-ring BLC compounds.

6. Single crystal XRD:

Single crystal X-ray diffraction data was collected using a Rigaku XtaLABmini X-ray diffractometer equipped with Mercury CCD detector with graphite monochromated Mo-Kα radiation (λ=0.71073 Å) at room temperature using ω scans. The data was reduced using Crystal Clear suite 2.0.and the space group determination was done using Olex2. The crystal structures were solved by using SHELXT and were refined using SHELXL97 through Olex2 suite. All the hydrogen atoms were geometrically fixed and refined using the riding model. Absorption correction was done by Multi-scan method.

The crystal structure below shows the ellipsoidal model of **2-4** using ORTEP where the probability level of the ellipsoid is 50%.

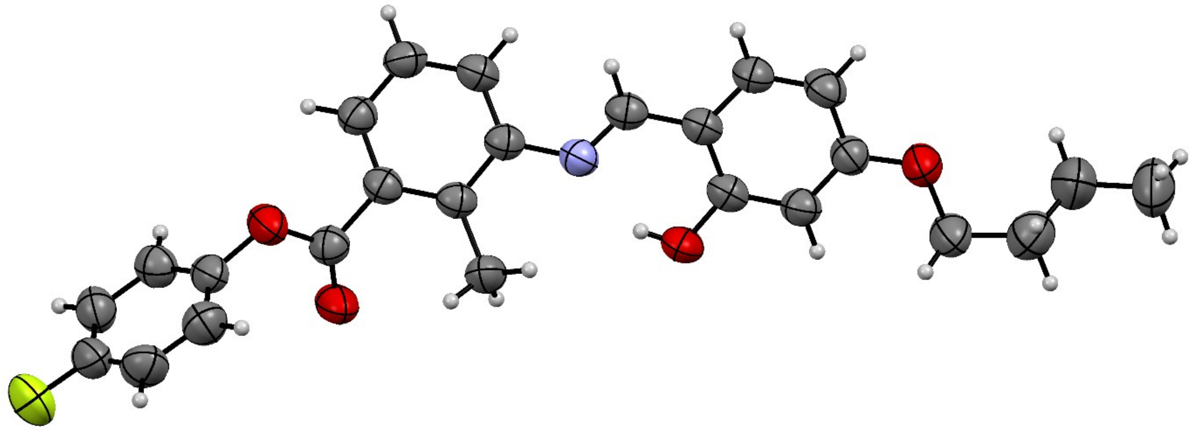


Figure S11: The crystal structure shows the ellipsoidal model of **2-4** using ORTEP where the probability level of the ellipsoid is 50%.

Table S2: Anisotropic Displacement Parameters ($\text{Å}^2\times10^3$) for **2-4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2\,[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	114.1(15)	81.1(12)	87.6(13)	-7.6(10)	9.1(11)	11.5(11)
O1	73.0(12)	57.5(11)	78.3(13)	10.8(9)	-6.8(10)	17.6(9)
O2	77.1(13)	60.0(11)	93.3(15)	10.4(10)	-8.2(11)	25.9(10)
O3	68.2(11)	46.8(10)	92.5(14)	18.2(9)	14.9(10)	18.8(8)
O4	68.4(12)	57.4(11)	92.7(14)	16.3(10)	-2.1(10)	9.3(9)
N1	60.0(12)	51.0(12)	59.1(12)	16.7(9)	14.1(10)	12.6(9)
C1	67.2(17)	66.4(17)	65.8(17)	5.1(14)	3.5(14)	15.7(14)
C2	72.8(17)	62.3(17)	74.3(19)	19.7(15)	5.2(15)	3.3(14)
C3	72.3(16)	69.0(17)	56.5(15)	19.6(13)	9.6(13)	15.2(14)
C4	57.0(14)	59.7(15)	60.4(16)	12.7(12)	-1.8(12)	14.5(12)
C5	70.6(17)	79(2)	84(2)	25.2(17)	22.2(16)	12.0(15)
C6	75.9(18)	95(2)	69.1(18)	16.4(17)	24.0(15)	21.8(17)
C7	57.0(14)	57.4(14)	60.1(15)	23.1(12)	9.8(12)	11.2(12)
C8	60.3(14)	50.2(13)	54.0(14)	20.8(11)	12.0(11)	13.2(11)
C9	58.4(14)	49.3(13)	57.3(14)	22.5(11)	15.1(11)	15.1(11)
C10	56.5(13)	51.0(13)	55.6(14)	21.5(11)	13.8(11)	14.1(11)
C11	67.9(15)	51.5(14)	59.8(15)	18.3(11)	19.2(12)	17.7(12)
C12	57.3(14)	64.3(16)	72.2(17)	26.6(13)	21.7(13)	20.4(12)
C13	55.5(14)	56.1(14)	68.1(16)	25.6(12)	12.4(12)	11.0(11)
C14	59.3(14)	60.9(16)	80.4(18)	15.7(14)	22.2(13)	13.0(12)
C15	63.1(14)	55.7(14)	58.5(14)	24.4(12)	15.3(12)	17.9(12)
C16	61.0(14)	49.1(13)	50.7(13)	18.8(11)	15.2(11)	14.2(11)
C17	67.1(15)	48.9(13)	53.7(14)	17.9(11)	17.1(12)	15.0(11)
C18	61.0(14)	55.2(14)	60.7(15)	19.3(12)	12.9(12)	16.8(12)
C19	62.5(14)	53.8(14)	58.4(14)	17.7(12)	8.9(12)	9.6(12)
C20	75.4(17)	47.3(14)	73.3(17)	20.1(12)	14.9(14)	16.1(13)
C21	62.2(15)	52.2(14)	67.7(16)	20.9(12)	13.5(13)	17.4(12)

C22	70.9(18)	67.0(17)	88(2)	20.1(15)	-3.6(15)	14.6(14)
C23	74.2(19)	104(2)	89(2)	35(2)	10.0(17)	15.7(18)
C24	80(2)	103(3)	123(3)	8(2)	3(2)	8(2)
C25	89(2)	86(2)	145(4)	31(2)	-14(2)	-9.4(19)

Table S3: Selected bond lengths (Å) and angles (°) for compound 2-4 in the crystal (atomic numbering see Fig. 6a of main paper)

Atoms	Bond Lengths	Atoms	Bond Angles
F1-C1	1.356	F1-C1-C2	118.31
C1-C2	1.360	F1-C1-C6	118.98
C2-C3	1.376	C6-C1-C2	122.71
C3-C4	1.369	C1-C2-C3	118.84
C4-C5	1.368	C2-C3-C4	119.04
C5-C6	1.376	C3-C4-C5	121.43
C6-C1	1.357	C4-C5-C6	119.40
C4-O1	1.408	C5-C6-C1	118.58
O1-C7	1.348	C4-O1-C7	118.08
C7-O2	1.190	O1-C7-O2	122.17
C7-C8	1.490	O2-C7-C8	126.73
C8-C13	1.393	O1-C7-C8	111.05
C13-C12	1.373	C7-C8-C13	117.78
C12-C11	1.372	C7-C8-C9	120.59
C11-C10	1.392	C9-C8-C13	121.48
C10-C9	1.406	C8-C13-C12	119.81
C9-C8	1.395	C13-C12-C11	119.78
C9-C14	1.505	C12-C11-C10	121.14
C10-N1	1.413	C11-C10-C9	120.03
N1-C15	1.279	C10-C9-C8	117.57
C15-C16	1.437	C10-C9-C14	119.59
C16-C17	1.401	C8-C9-C14	122.78
C17-C18	1.384	C10-N1-C15	122.29
C18-C19	1.386	C15-C16-C17	121.42
C19-C20	1.394	C15-C16-C21	120.80
C20-C21	1.360	C17-C16-C21	117.78
C21-C16	1.400	C16-C21-C20	121.74
C17-O3	1.343	C21-C20-C19	119.78
C19-O4	1.355	C20-C19-C18	120.12
O4-C22	1.436	C19-C18-C17	119.60
C22-C23	1.533	C18-C17-O3	117.65
C23-C24	1.443	C16-C17-O3	121.41
C24-C25	1.519	C19-O4-C22	118.90

Table S4: Selected bond lengths (Å) and angles (°) for compound SB-C8 in the crystal (atomic numbering see Fig. 7a of main paper):

Atoms	Bond Lengths	Atoms	Bond Angles
O1-C8	1.302	C8-O1-H1	109.49

O2-C8	1.200	O1-C8-O2	123.60
C8-C3	1.497	O2-C8-C3	121.94
C3-C2	1.399	O1-C8-C3	114.43
C2-C1	1.401	C2-C3-C4	120.32
C2-C7	1.501	C2-C3-C8	124.58
C1-C6	1.387	C8-C3-C4	115.09
C6-C5	1.369	C3-C4-C5	121.42
C5-C4	1.371	C4-C5-C6	119.55
C4-C3	1.388	C5-C6-C1	119.82
C1-N1	1.405	C6-C1-C2	122.00
N1-C9	1.313	C6-C1-N1	121.30
C11-O3	1.295	C2-C1-N1	116.69
C9-C10	1.393	C1-C2-C3	116.87
C10-C11	1.429	C1-C2-C7	119.79
C11-C12	1.398	C3-C2-C7	123.31
C12-C13	1.370	N1-C9-C10	122.76
C13-C14	1.415	C1-N1-C9	128.83
C14-C15	1.347	C9-C10-C11	121.10
C15-C10	1.414	C9-C10-C15	120.12
C13-O4	1.350	C11-C10-C15	118.78
O4-C16	1.433	C10-C15-C14	121.47
C16-C17	1.488	C15-C14-C13	119.55
C17-C18	1.507	C14-C13-C12	120.93
C18-C19	1.506	C13-C12-C11	120.51
C19-C20	1.513	C12-C11-C10	118.76
C20-C21	1.502	C12-C11-O3	121.67
C21-C22	1.516	C10-C11-O3	119.57
C22-C23	1.499	C14-C13-O4	114.50
		C12-C13-O4	124.57
		C13-O4-C16	118.03

Table S5: Selected molecular parameters of compound 2-4 and SB-C8 in the crystal structure (atomic numbering see Fig. 6a and 7a of main paper):

Compund	O-H...N	O-H/Å	H...N/Å	O...N/Å	Angle O-H...N/°
2-4	O3-H3...N1	0.820	1.852	2.581	147.53
SB-C8	O3-H1...N1	1.683	0.988	2.537	142.27
Compound	O-H…O	O-H/Å	H-O/Å	O-O/Å	Angle O-H...O/°
SB-C8	O1-H1...O3	0.820	1.695	2.508	171.06

7. <u>Density functional calculation</u>:

Table S6: DFT calculated molecular parameters for all the compounds of 1-n and 2-n series.

Compound	**Molecular length (Å)**	**Dipole moment (Debye)**	**Bent angle (˚)**
1-4	22.74	4.98	147
1-6	25.18	5.04	147
1-8	27.61	5.07	147

1-10	30.04	5.11	147
1-12	32.48	5.13	147
2-4	22.30	4.32	146
2-6	24.74	4.37	146
2-8	27.20	4.43	147
2-10	29.62	4.46	146
2-12	32.06	4.49	147

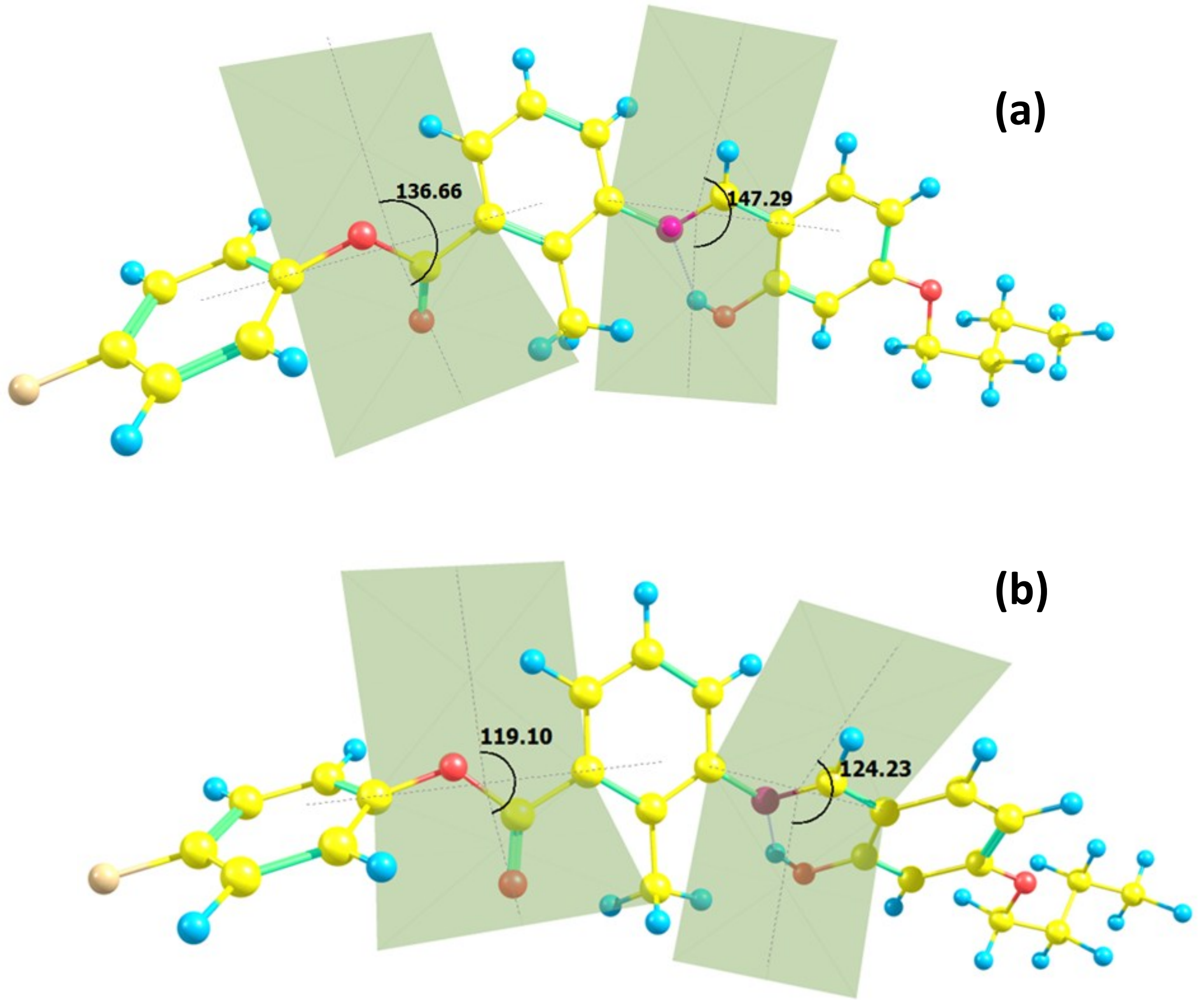


Figure S12. Molecular architecture of 2-4 exhibiting torsional angle between the rings (a) in crystal structure (b) in DFT optimised geometry.

8. Materials and reagents:

Chemicals and solvents were all of AR quality and were used without further purification. 2, 4-Dihydroxybenzaldehyde, 3-Amino-2-methylbenzoic acid, 4-Fluorophenol and 4-Chlorophenol were all purchased from TCI (Japan). N, N- dicyclohexylcarbodiimide (DCC) was purchased from Fluka Analytical and 4-dimethylaminopyridine (DMAP) from Sigma Aldrich. Column chromatographic separations were performed on silica gel (60-120 mesh).

Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254).

9. Instrumental:

Structural characterization of the compound was carried out through a combination of FT-IR (Infrared Spectroscopy-Perkin Elmer Spectrum AX3), ^{1}H-NMR and ^{13}C-NMR (BrukerBiospin Switzerland Avance-iii 400 MHz and 100 MHz spectrometers respectively), UV-VIS-NIR spectrophotometer (LABINDIA UV-Vis Spectrophotometer 3000+) and Mass Spectrometry (Waters synapt g2s). NMR spectra were recorded using deuterated chloroform

($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal standard.

Differential Scanning Calorimetry (DSC) measurements were performed on Perkin Elmer DSC 8000 coupled to a Controlled Liquid Nitrogen Accessory (CLN 2) with a scan rate of 5°C/min.

Polarising Optical Microscopy (POM) textural observations of the mesophase were performed with Nikon Eclipse LV100POL polarising microscope provided with a Linkam heating stage (LTS 420). All images were captured using a Q-imaging camera.

X-ray Diffraction (XRD) studies were carried out on the samples using Cu Kα (λ=1.54 Å) radiation from GeniX3D microsource, using Pilatus 200K detector in Xeuss 2.0 SAXS/WAXS system.

10. References

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